Research Proposal

Proposed Title of Work:"Quantum chemical investigation of phosphorescent organometallic complexes used in organic light emitting diodes"

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Abstract: Organic light emitting diodes (OLED), operating on the principles of electroluminescence, are emerging as the leading technology for display units of electronic devices. Identification of novel phosphorescent materials is the key to prepare OLEDs with high luminous efficiency. Moreover, to achieve full colour display OLED materials are requiredhave full colour tuning property. The focus of our research is to identify materials emitting blue light with high efficiency. However, a great challenge remains in identifying right organic materials that provide bright blue phosphorescence as it requires a larger energy gap between the excited triplet and the ground state. It has been observed that organometallic complexes of heavier transition metals (e.g., Ir) often show blue phosphorescence. Over the last few years many Iridium complexes have been synthesized and characterized to manifest blue phosphorescence property.With the development of computational chemistry,the reliability and accuracyof computational prediction of chemical and physical properties of moderate to large organometallic complexes are now widely recognised. Therefore, systematic investigation of the effects of ligands on the emission spectra of Ir complexes by (i) changing the entire ligand structure (ii) changing the nature of the substituted functional groups (electron donating/electron withdrawing) or the positions of functional groups attached to the ligand is carried out in this work. This understanding would enable accurate prediction of the ideal choice of ligands in order to maximizetheefficiency of the phosphorescence emitters that can be used as OLED materials.

Introduction:

Organic light emitting diodes (OLED) are increasingly gaining popularity in display technology due to their power efficiency, low cost and better aesthetics. OLEDs rely on the phosphorescence property of organic materials. To achieve complete colour display it is therefore required to have green, red and blue phosphorescence materials. Recently many organic materials have been synthesised and computationally analysed for green and red phosphorescence. However, a great challenge remains in identifying right organic materials that provide bright blue phosphorescence as it requires a larger energy gap between the excited triplet and the ground state to obtain this emission wavelength. It has been observed that organometallic complexes of heavier transition metals often show blue phosphorescence, of which, Iridium complexes have been so far the most promising ones. Over the last few years many Iridium complexes have been synthesized and characterized to manifest blue phosphorescence property.

The successful applications of Iridium complexes in OLEDs are primarily due to two factors: (i) the Iridium atom has large d-orbital splitting compared to other heavy metals, and (ii) the closely lying π–π* and metal to ligand charge transfer (MLCT) states together with the heavy atom effect enhances the spin-orbit coupling and intersystem crossing, thus increasing the efficiency of phosphorescence. The modulation in ligand structures is expected to have a profound effect on both emission colour and phosphorescence quantum efficiency. Therefore, the knowledge about ideal ligand structures and their appropriate chelate positions could guide the synthesis of best suited organometallic complexes for blue light generation.

With the development of computational chemistry, the reliability and accuracy of computational prediction of chemical and physical properties of moderate to large organometallic complexes are now widely recognised. This makes in silico prediction of potential OLED materials an attractive field of research. In this research, computational investigation of structural and spectroscopic properties of Ir-based

organometallic complexes will be carried out which would help understanding the electronic origin of the blue phosphorescence of Ir complexes. This understanding would enable accurate prediction of the ideal choice of ligands and solvent media in order to maximize the efficiency of the OLED materials. To this end, we propose to carry out ab initio electronic structure calculations of a series of cyclometalated Ir complexes by employing density functional theory (DFT) calculations of ground and excited states of the complexes both in vacuum and in solvents with varying dielectric constants. We aim to achieve a detailed understanding of the absorption and emission properties of these complexes with the help of time-dependent version of DFT. We propose to investigate the role of ligand substitution on the emission properties of the complexes and strive to facilitate the discovery of highly efficient blue light emitting materials.

Objectives:

Organic light emitting diodes (OLED), operating on the principles of electroluminescence, are emerging as the leading technology for display units of electronic devices [1-4]. Identification of novel phosphorescent materials is the key to prepare OLEDs with high luminous efficiency. Moreover, to achieve full colour display OLED materials are required to have green, red and blue phosphorescence property. The focus of our research is to identify materials emitting blue light. To this end, we consider Iridium based organometiallic complexes with strong ligand-field strength, which are expected to emit high energy blue light. The strong spin-orbit coupling of Iridium along with the presence of large ligand-field splitting instigates the high energy emission. In particular, we propose to use computational methods to understand the role of different ligands and solvents on colour tuning of OLED materials based on Iridium cyclometalated complexes, with the following specific objectives:

- Computational study of the emission spectra of different Ir-based blue complexes (outlined in methodology section) in terms of their oscillator strength and quantum efficiency.

- Investigation of the effects of ligands on the emission spectra of Ir complexes by (i) changing the entire ligand structure (ii) changing the nature of the substituted functional groups (electron donating/electron withdrawing) or the positions of functional groups attached to the ligand.

- Understanding the role of solvation on the emission spectra of Ir-based complexes.

- Computational prediction of novel Ir-based complexes with high potential of efficient blue OLED materials that would motivate the synthesis and characterization by experimentalists.

Methodology:

In this work we propose to carry out electronic structure calculations of various Ir based complexes and determine their emission spectra, with a special emphasis on the roleof solvation and the role of the substituents of the ligands.

(i) **Effect of ligands on phosphorescence:** The Iridium biscarbene complexes, shown in Fig. 1, differ by the choice of different heteroleptic N^N ligands which influences their phosphorescent property substantially (from red to green to deep blue) [5]. The emission energy of Iridium biscarbene complexes can be tuned over a wide range varying from 455 to 599 nm. The devices using $(fpmi)_2Ir(dmpypz)$, $(mpmi)_2Ir(dmpypz)$, $(mpmi)_2Ir(pybi)$, and $(mpmi)_2Ir(priq)$ as dopant emitters show excellent external

quantum efficiency of 17.1, 15.4, 24.4, and 24.9%, respectively [5]. So far, an accurate theoretical interpretation of these effects is lacking.

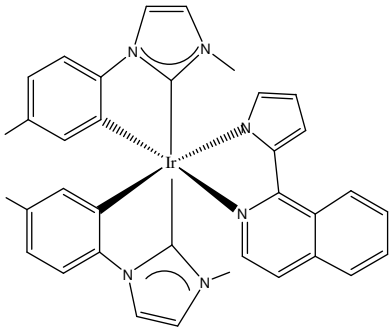
The origin of phosphorescence is typically attributed to a triplet MLCT (metal to ligand charge transfer) excited state. In the presence of electron-withdrawing ligands the decrease in the energy of the triplet ππ* states may also contribute to the emission. Therefore, emission is considered to be a mixture of both MLCTand IL (intraligand) character [1]. On the other hand, the incorporation of electron-rich ligands raises the energy of the lowest excited state, thus increasing the HOMO-LUMO energy gap and resulting in a blue-shift of the emission wavelength when compared to the parent complex.

We propose to computationally investigate the effect of ligand substitution on the photo-physical property of the cyclometalated Ir complexes using DFT and TD-DFT methods so as to provide a detailed computational support for the experimental observations (Fig. 1). It is very clear that the colour tuning depends on the choice of ligand. We propose to carry out two ways of performing ligand substitution:

(1) Changing the entire ligand (Fig. 2 (a)),
(2) Changing the functional groups attached to the ligands (Fig. 2 (b)).

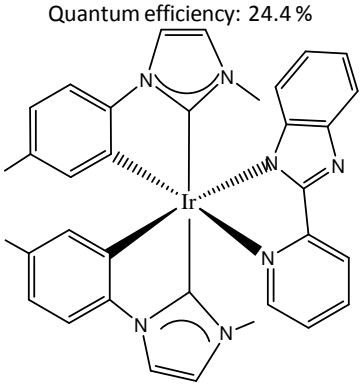
For the first kind of ligand substitution, we would like to introduce the electron withdrawing ligand, e.g., CN, in place of metallacyclic ligand as shown in Fig. 2(a). For the second kind of ligand substitution, we would replace the F atom with some equal or more electron withdrawing groups like CN, CF_3, CO etc., as shown in Fig. 2(b).

Emission Wavelength: 599 nm, Red
Quantum efficiency: 24.9 %



$(mpmi)_2Ir(priq)$

Emission Wavelength: 530 nm, green
Quantum efficiency: 24.4 %



$(mpmi)_2Ir(pybi)$

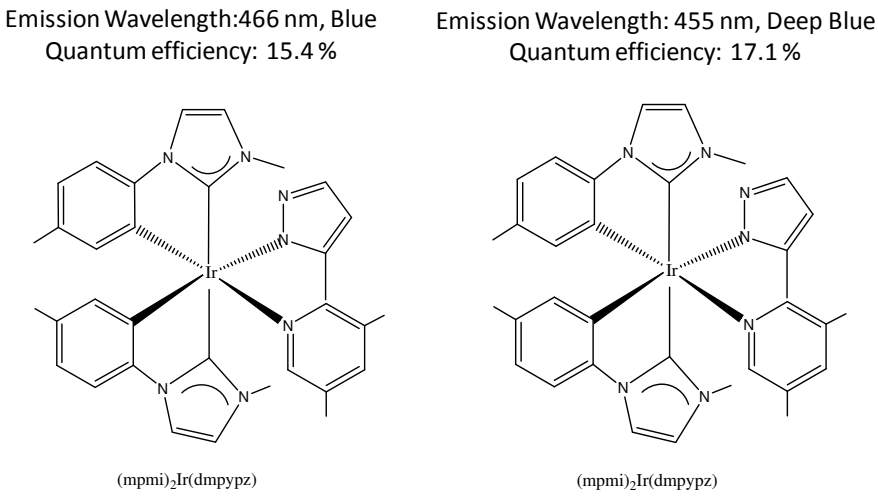


Fig. 1: The effect of ligands on the phosphorescence of the Ir biscarbene complexes. The four Iridium biscarbene complexes shown, have different heteroleptic N^N ligands and exhibit a broad range of emission (455 nm to 599 nm) [5].

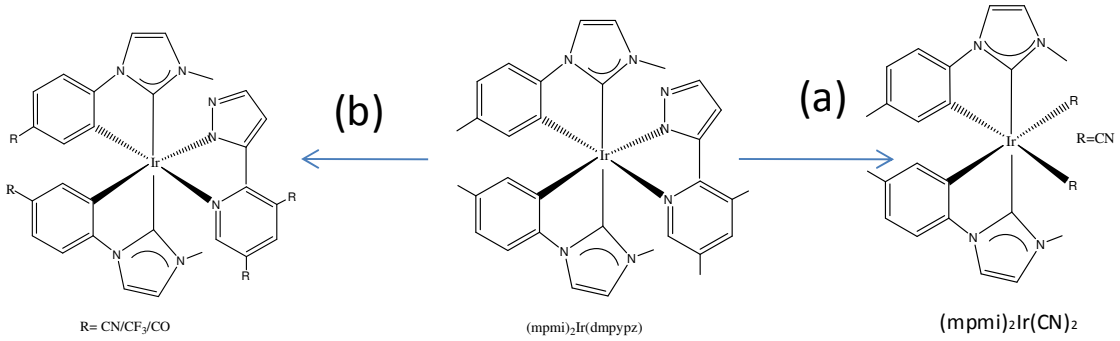


Fig 2: Proposed investigation of the role of ligand substititution on the emission spectra. (a) dmpypz ligand is replaced by cyanide. (b) Substitution of electron withdrawing group attached to the cyclometallated ligands.

We would then analyze the effects of ligand substitution on the colour tuning by carying out electronic structure calculations of the ground and excited states of the concerned Ir complexes.This will enhance the systematic understanding of ligand substitution on OLED colour tuning for blue phosphorescence.

(ii) **Solvent effects on the ground and the excited states:** Two blue emitting cationic Iridium complexes (shown in Fig. 3) with N-heterocyclic carbene-pyridine as the ancillary ligand, namely, $[Ir(ppy)_2(pymi)]PF_6$ and $[Ir(dfppy)_2(pymi)]PF_6$ have been shown to exhibit blue light emission with peaks at 472 and 451 nm, respectively, in CH_3CN solution. However, the OLEDs based on the same two materials give blue-green electroluminescence in thin film (506 and 482 nm, respectively) [6], suggesting a strong influence of solvent on the phosphorescence property and the subsequent colour tuning of the OLED material. However, a detailed understanding of the origin of the solvent effects at the electronic level is missing [6].

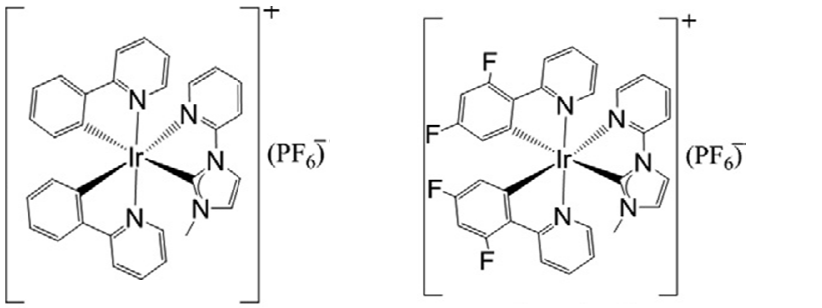

Solvent: CH3CN
Emission Wavelength : 472 nm, Blue
In Thin Film
Emission Wavelength : 506 nm, Greenish-blue
Solvent: CH3CN
Emission Wavelength : 451 nm, Deep Blue
In Thin Film
Emission Wavelength : 482 nm, Blue-green

Fig. 3: Solvent effects on the phosphorescence of Ir complexes. The cationic Iridium complexes with N-heterocyclic carbene-pyridine as the ancillary ligands exhibit very different emission wavelengths in CH_3CN and in thin films [6].

We propose to carry out a systematic investigation of the role of the solvent on the relative stabilization of the ground and the excited states of the Ir complexes. The effect of solvent will be studied through the well known PCM (polarization continuum model) method [7, 8] by varying solvent dielectric constants to take into account the effect of solvents like CH_3CN, DMSO, water, and acetone. The role of the solvents on the equilibrium geometry and energy of the excited states will be a useful method to determine quantum efficiency of the Ir complexes in different solvents.

To achieve the above two research objectives, i.e., the role of solvent and ligands in the emission spectra of Ir complexes, we would carry out electronic structure calculations of the concerned complexes in their ground and excited states with the following technical details:

1. Characterization of the ground states of Ir complexes: We will carry out standard density functional calculations (Gaussian09 [9]software) with an exchange correlation functional with density gradient corrections as proposed by Becke and Perdew (BP86) to optimize the ground state geometries. BP86 will be used with Resolution of the Identity (RI) approximation to facilitate faster computation. We will validate our results with single-point calculations using B3LYP functionals. We will employ double-ζ quality 6-31G** basis set for the lighter non-metallic atoms (such as C, N, F, O and H atoms) and the LanL2DZ basis set for the Ir atom. To reduce computational cost and to account for relativistic spin-orbit effects, we would consider the relativistic effective core potential (ECP) for Ir which replaces the inner core electrons leaving the outer layer [$5s^2 5p^6$] electrons and the ($5d^6$) valence electrons. These basis sets are adequate to describe the ground state geometry of the Ir(III) complexes, as has been verified and discussed in the literature [10]. All the optimised structures will be confirmed by the evaluation of Hessian matrix. Analytical evaluation of the Hessian matrix will confirm the nature of minima of potential energy surface stationary points associated with the optimised structures.

2.Calculation of the singlet-triplet or singlet-singlet excitation energies with a time dependent DFT (TD-DFT) approach: To understand the photo phosphorescence property of Ir-complexes, we need to perform excited state analysis. While the multi-reference quantum chemical methods are best suited to study the excited state properties, these calculations are prohibitively expensive for the metal-ligand complexes considered in the proposed work. On the other hand, recently time dependant density functional theory has become very effective in realizing excited state representation of medium to large size molecules [4].

The classic density functional theoryformalism introduced by Hohenberg, Kohn, and Sham in the mid-1960s is based on the idea that the complicated *N*-electron wave function can be replaced with the mathematically simpler 1-electron charge density in electronic structure calculations of the ground stationary state. As such, ordinary DFT cannot treat time-dependent (TD) problems nor describe excited electronic states. In 1984, Runge and Gross proved a theorem making TD-DFT formally exact [11]. Information about electronic excited states may be obtained from this theory through the linear response (LR) theory formalism [4]. Beginning in the mid-1990s, LR-TD-DFT became increasingly popular for calculating absorption and other spectra of medium- and large-sized molecules [12]. Its ease of use and relatively good accuracy has now brought LR-TD-DFT to the forefront for this type of application.

TD-DFT calculation of phosphorescence materials will help us to understand its absorption spectra, provide tools to carry out excited state geometry and finally predict the emission spectra. It also provides additional insight on the charge transfer characteristics upon excitation, geometry modifications and distribution of high-lying excited states. All TD-DFT calculations for our purpose will be performed with a fairly large basis set: Stuttgart relativistic small-core effective potential for Iridium; double-ζ plus polarization basis set (cc-pVDZ) for the C, F, O N and hydrogen atoms. The PBE0 exchange-correlation functional (casting 25% of exact Hatree-Fock exchange into the PBE exchange-correlation functional) will be considered for TD-DFT calculations. This step provides us the means to evaluate the absorption spectrum.

3. Geometric characterization of the excited state: The geometries of the lowest triplet excited state of cyclometalated Iridium complexes can be evaluated by the unrestricted PBE0 (uPBE0) formalism with triplet spin multiplicity, without assuming any symmetry constraints. Earlier research has shown that the PBE0/LanL2DZ;6-31G** level of theory is adequately accurate and affordable to evaluate both ground and excited state geometries for the transition metal systems. We would explore different combinations of functionals and basis sets.

Expected Outcome:

Within the research work we aim to obtain:

1. A clear understanding of the influence of solvents and ligands with different electronic properties on the geometry and energy levels of the ground and excited states of Ir complexes.

2. Emission spectra of a variety of Ir complexes with detailed information on the oscillator strength, quantum efficiency, and charge distribution.

3. Prediction of efficient blue-emitting materials based on organometallic complexes of Iridium in appropriate solvents.

4. A robust computational framework to carry out excited state analysis of OLED emitter materials with or without solvent.

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